

SENSITIZED PHOSPHORESCENCE OF ORGANIC MOLECULES
AT LOW TEMPERATURE

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INTERMOLECULAR ENERGY TRANSFER WITH AN

EXCITATION OF A TRIPLET LEVEL

Acad. A. N. Terenin and V. L. Yermolayev

In an investigation into the excitation energy transfer in mixture solutions of fluorescent aromatic molecules at liquid air temperature we have succeeded in establishing the phenomenon of sensitized excitation of one compound of the phosphorescent spectrum by another (1).

A mixture of two fluorescent substances A and B produced by a condensation of their vapors in a vacuum onto a surface cooled by liquid air (2), or by the dissolving and then freezing an alcohol solution, is subjected to excitation by a monochromatic light extending into the region of a longer-wave absorption spectrum, such as spectrum B for example. The latter is definitely not overlapped by the absorption spectrum of the second A component whose absorption begins only with shorter wave lengths. Thus the ordinary fluorescent (and phosphorescent) spectrum of the A molecules cannot be excited. But in the presence of compound B, which is capable of absorbing an exciting light, a luminosity (phosphorescence) of long duration originating from the metastable, that is the triplet level* of molecule A, emerges in the A + B mixture. That level lies lower than the excited (fluorescent)

*Although the concept of the triplet-biradical origin of the metastable level was substantiated by one of the authors (A. I. Terenin) back in 1943 (3) to counteract the hypothetical "tautomer" of the molecule introduced by Frank and Livingston (4), one year before Lewis and Kasha (5), the recently published book Th. Forster: *Fluoreszenz Organischer Verbindungen*, 1951, (p. 227), in outright contradiction to the facts, credits A. N. Terenin with the defense (1) of the Frank and Livingston concept which he had repeatedly opposed in the press (3 and 6).

singlet level of molecule A, and is in this case accessible to excitation by way of an energy transfer from the molecules B which are initially excitable by light.

The above-described phenomenon was first detected in the following mixture: naphthalene (A) + benzaldehyde (B). It follows from Fig. 1 that the benzaldehyde absorption spectrum shifted a considerable distance toward the long waves from the beginning of the naphthalene absorption spectrum*. In line with this, the excitation of a frozen layer or solution of naphthalene alone by a filtered radiation of 3663 \AA (1) revealed no emission in the near ultraviolet and visible regions. The addition of a small quantity of benzaldehyde, however, is followed by the appearance of a characteristic visible spectrum of naphthalene phosphorescence. Shown in Fig. 2 (see inset on p. 640) [not supplied to the translator] are the photographs of the afterglow spectra (1). A comparison of the frequencies of the afterglow bands we observed with the long known phosphorescent naphthalene spectra at liquid air temperature is shown in Table 1.

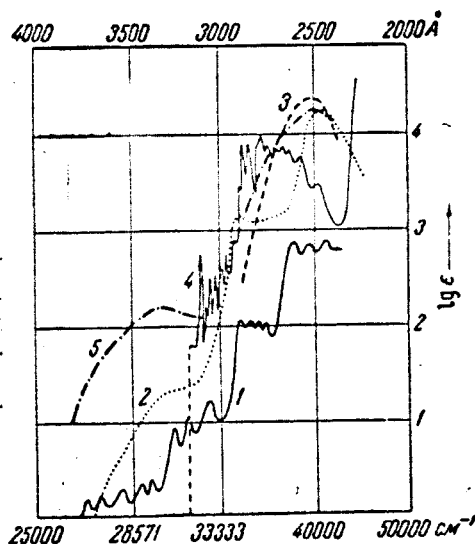


Fig. 1. Absorption spectra: 1-benzaldehyde dissolved in a pentane propane mixture at -180° (9) (because of the lack of information, the height of the bands is arbitrary and obviously understated); 2-benzaldehyde in ethanol at $+20^{\circ}$ (10); 3-diaphenyl in an ethanolmethanol mixture at -180° (11); 4-naphthalene in an ethanol-methanol mixture at -180° (7, 11); 5-benzophenone in ethanol at $+20^{\circ}$.

* According to L. A. Blumenfel'd [7], the extreme long-wave band of the absorption spectrum of a naphthalene solution in ethanol is at 3270 \AA , and is considerably weakened at a lower temperature.

We have observed such an effect of phosphorescence sensitization in the case of the following pairs of substances in which the first is a compound primarily excitable by light and absorbing a radiation of 3663 Å: benzaldehyde' + diphenyl (Fig. 2, see inset on p. 644), benzophenone' + naphthalene and benzophenone' + diphenyl. Judging by the very shortwave band of the glow spectrum, the light-excitable benzaldehyde level which emits its characteristic spectrum (2) is located at an altitude of $25,200\text{ cm}^{-1}$, that is higher than the triplet levels of naphthalene ($21,300\text{ cm}^{-1}$) and diphenyl ($22,800\text{ cm}^{-1}$) (8, 5). The excited as well as the triplet level of benzophenone ($24,400\text{ cm}^{-1}$) (5) is higher than the triplet levels of naphthalene and diphenyl.

The possible explanation of the shifting naphthalene absorption spectra and other A components in the long-wave direction as a result of the association with the added second component B (benzaldehyde, etc.) is contradicted by the coincidence of the substance A spectrum, observable in such a sensitized phosphorescence, with its ordinary phosphorescence spectrum (see Table 1). Furthermore, this phenomenon does not occur in the case of added polar molecules capable of a higher degree of association than benzaldehyde or benzophenone but not possessing an absorption spectrum in the region of exciting radiation 3663 Å, as for example: benzoic acid, acetaldehyde, formaldehyde, benzonitrile, diphenylamine, formamide and nitrobenzene. None of these in combination with naphthalene had the effect produced by benzaldehyde and benzophenone.

The growing intensity of the sensitized naphthalene phosphorescence, depending on its concentration in a mixed benzaldehyde + naphthalene solution, with a constant concentration of benzaldehyde $4 \cdot 10^{-2}$ mole/liter, is linear in nature (see Fig. 3a). The changing range of the naphthalene concentration was between $5 \cdot 10^{-3}$ and $8 \cdot 10^{-2}$ mole/liter. Shown in Fig. 3a also for the mixed benzaldehyde + diphenyl solution is the relationship between the diphenyl phosphorescence intensity

Table 1

Naphthalene phosphorescence spectrum (in cm^{-1})

Band No.	0	1	2	3	4	5	6
According to Goldshteyn (8) . . .	{ 21240 21150	20700	19800	19600 19325	18525 18355	16950	15830 15400
According to Lewis and Kasha (5) . .	21300	20800	19830	19420	18450	17050	15700
Sensibilized phosphorescence . .	21190	20620	19660	fused with pre- ceding	18080	16870	15300

(indicated as +++) and its concentration which is also linear in appearance.

Fig. 3b shows that the increasing concentration of naphthalene to a level approximately above 10^{-2} mole/liter results in the diminishing intensity of benzaldehyde emission (which had a constant concentration of $4 \cdot 10^{-2}$ mole/liter), and that is as it should be if the benzaldehyde transfers its excitation energy to naphthalene. The intensity values of the benzaldehyde luminosity produced by constant excitation without a phosphorescope (as observed through crossed light filters) are indicated by cross checks. The dotted curve drawn through them can be described by the formula $I = I_0 (1 - bc_N)$ (c is the naphthalene concentration, and b the empirical constant) which is deduced from the assumption of the proportionality between the excited benzaldehyde molecules, which had transferred their energy to the naphthalene molecules, and the concentration of the latter. The reduction of the benzaldehyde phosphorescence intensity for a later stage of attenuation, obtained by the use of a slow phosphorescope, is indicated by circles and a solid curve.

In the physical attenuation processes, the reduction in the luminescence yield should be accompanied by a parallel reduction in lifetime τ of the excited molecules. The numerous measurements of the naphthalene effect on the phosphorescence duration of the energy donor, benzaldehyde, revealed that the τ of the latter

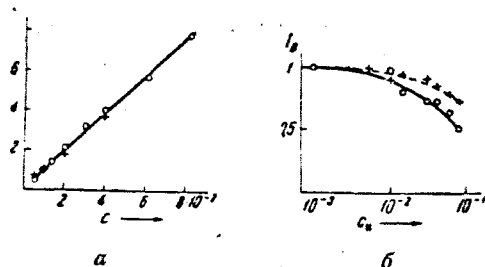


Fig. 3. a-intensity of sensitized naphthalene and diphenyl phosphorescence depending on their concentration c (mole/liter); benzaldehyde concentration const. $= 4 \cdot 10^{-2}$; $\circ\circ\circ$ naphthalene; $+++$ diphenyl; b-the attenuation of benzaldehyde phosphorescence by naphthalene depending on the naphthalene concentration c_N ; $c_B = \text{const.} = 4 \cdot 10^{-2}$.

(0.10 sec.) is reduced by the highest naphthalene concentration ($8 \cdot 10^{-2}$) only 5%, whereas the intensity of the benzaldehyde shows a 25% drop. Such a disparity is frequently observed also in the attenuation of the usual fluorescence in solutions by extraneous and inherent molecules. The average distance between the benzaldehyde and naphthalene molecules, assuming the highest concentration of the latter, amounts to 20 \AA which is slightly longer than their combined radius.

Finally, Fig. 4 shows the relationship between the intensity of the naphthalene phosphorescence and the concentration of the energy donor, benzaldehyde, as measured by a slow phosphoroscope, with the naphthalene concentration remaining constant at 10^{-2} mole/liter. The benzaldehyde phosphorescence intensity measured at the same time with a fast phosphoroscope yielded some values that can easily be plotted on the same curve. This general dependence can be reproduced by the formula for the absorbable energy of exciting radiation: $I_c = I_{\text{pred}} (1 - e^{-ac})$, where c is the concentration of light-absorbing benzaldehyde, I_c and I_{pred} are the intensities of benzaldehyde (of various concentrations) emission proportional to the absorbable energy, and a is a constant. The fact that the intensity of the energy acceptor, naphthalene, fits into the same formula shows that the number of transfer events is proportional to the number of excited molecules of the energy donor, that is benzaldehyde. A concentration of the latter on the order of 10^{-1} mole/liter produces a complete absorption of the exciting light, and the number of its molecules

assumes a constant value. The intensity of the naphthalene phosphorescence in this case also reaches a saturation point, and the luminosity of both components is drawn to the front wall through which the exciting radiation enters.

The metastable benzaldehyde level, from which its phosphorescence spectrum is emitted and the energy transferred to other molecules, is apparently a triplet rather than a singlet level reached by the absorption of light in its long-wave weak band system (12). The maximum absorption coefficient and the area occupied by this band system are used for computing the lifetime τ of the excited level which is considerably shorter than the observable duration of the benzaldehyde phosphorescence. The absence of any emission from the single level may be explained by the fact that the change from there to the triplet level is very rapid, as is the case with diacetyl phosphorescence in vapor (13).

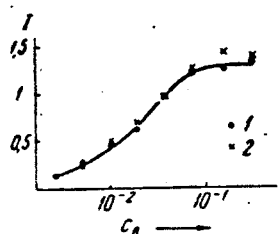


Fig. 4. The intensity of sensitized phosphorescence of naphthalene (1) and phosphorescence of benzaldehyde (2) as a function of benzaldehyde concentration.

We have thus established the transfer of energy from the light-excited molecules to other molecules of a different type, including the direct transfer of the latter to a triplet level.

The identity of the concentration depolarization curves representing the fluorescence and phosphorescence of dyestuffs, as well as the lack of a diminution in the polarization in the course of the phosphorescence attenuation, have prompted P. P. Feofilov to assume that it is impossible to transfer the energy from a metastable molecule to another one of the same type, in its basic state (14). Other authors (15), however, have found that the life-time of phosphorescent

molecules is reduced by an increase in their concentration, which suggests the possibility of such an energy transfer. This problem calls for a further study.

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3 May 1952.

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